Nuclear Magnetic Resonance Spectra of Alkyldiboranes

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Abstract: H^1 and B^{11} nmr spectra have been measured for a variety of mono- and dialkyldiboranes, including three cyclic organodiboranes. Chemical shifts and coupling constants of terminal and bridge hydrogens attached to boron are systematically investigated with regard to the influence of alkyl substitution. Assignments and structural correlations are confirmed by means of B^{11} decoupling experiments. The high viscosity of poly(μ-trimethylene)diborane accounts for the intrinsic B^{11}–H^1 decoupling by its effect on B^{11} quadrupole relaxation. Generally, proton resonances of α-CH_2 groups attached to boron are found upfield from chemical shifts of alkane methylene protons.

The most useful physical method for expeditious structural studies of alkyldiboranes ($R_xB_2H_{6-x}$) is provided by nmr spectroscopy, as evidenced by the B^{11} spectral studies of Williams, *et al.*, on methyldiboranes.[1] However, the scarcity of H^1 nmr data[2–4] made it desirable to carry out the present investigation. Initial attention was directed at the following: (1) determination of the chemical shifts of alkyl protons (H_a) and the dependence of these shifts on boron substituent effects; (2) determination of the chemical shifts of terminal (H_t) and bridge (H_b) protons attached to boron, and the dependence of these chemical shift values on the number and position of neighboring alkyl groups; and (3) proton magnetic resonance confirmation of the H_t–B^{11} and H_b–B^{11} multiplet splittings (B^{11}, $I = {}^3/_2$) obtained from B^{11} nmr measurements.

Experimental Section

Materials. The alkyldiboranes were generally prepared by the gas-phase hydroboration of corresponding olefins as described in the previous paper.[5] Normally, spectra were obtained from pure, liquid samples sealed in 5-mm thick-wall nmr tubes under vacuum. For H^1 resonances, TMS was added as an internal standard.

Apparatus. Proton resonance spectra were recorded using a Varian A-60 spectrometer normally operated at ambient temperature. Boron-11 decoupling experiments[6,7] were performed at 19.2 Mc using an NMR Specialties Model HD-60 spin decoupler and a Hewlett-Packard Model 200 CD wide-range audio oscillator. Boron-11 nmr spectra were obtained with a Varian V-4300 high resolution nmr spectrometer operating at 12.83 Mc.

Results and Discussion

The results of our measurements of H^1 and B^{11} chemical shifts and coupling constants of alkyldiboranes are summarized in Table I; previously reported values for diborane, methyldiboranes, and 1,2-tetramethylenediborane are included for comparisons.

Resonances of Alkyl Protons (H_a). Among the proton resonance spectra of alkyldiboranes, the alkyl proton resonances of the cyclic compounds 1,2-tetramethylenediborane (IX)[4] and 1,2-(1′-methyltrimethylene)diborane (X) are readily assigned by making analogical comparisons to the H^1 nmr spectrum of 1,2-trimethylenediborane (VIII).[8] From area considerations (Figure 1) alone it is clear that the α-CH_2 protons of VIII resonate at considerably higher field than the β-CH_2 protons. Therefore, of the two H_a resonances of equal area displayed by IX, the high-field peak (τ 9.02) is assigned to the two boron-attached α-CH_2 groups. Similarly, a portion of the resonance at τ 8.99 for X is assigned to the lone α-CH_2 (the CH_3 resonance accounts for the remainder), and the peak at τ 8.68 to the lone β-CH_2 group.

Except for modest resolution of the lone β-CH_2 peak of VIII (triplet?), further splitting due to H_a–H_a spin interactions is not generally observed; however, all of the H_a resonances are rather broad. One explanation for this may be that the H_a protons are also coupled very weakly to the nearby boron atoms;[9,10] additionally, weak coupling is to be expected from H_a–H_t and from H_a–H_b spin interactions, which together may well have the effect of smearing coupling between α- and β-CH_2 protons. Also, viscosity effects (*vide infra*) cannot be entirely ignored.

Assigned chemical and internal shifts for methylene and methyl proton resonances of VIII, IX, X, and some noncyclic alkyldiboranes are correlated (ΔA, ΔB, ΔC) with alkanes in Table II. Since ΔB values of alkanes are of approximately the same magnitude as the upfield shift of α-CH_2 protons of VIII, IX, and X (*i.e.*, ΔA = *ca.* 0.3–0.6 ppm), it is to be expected that the methyl and α-methylene resonances of alkyldiboranes are nearly superimposed ($\Delta B \cong 0$). Indeed, the H_a resonances of $C_2H_5B_2H_5$, 1,1-$(C_2H_5)_2B_2H_4$, and of 1,2-$(C_2H_5)_2B_2H_4$ consist of one singlet only (Figure 2b). Also, as might be expected, protons attached to β carbons are much less affected by boron substituent effects than those of α carbons (*cf.* ΔC of X and of *n*-octane, Table II). It is then not unreasonable to assign the low-field H_a regions of IV and VII (compounds formed from diborane addition to

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(1) R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960).

(2) D. F. Gaines, R. Schaeffer, and F. Tebbe, *ibid.*, **67**, 1937 (1963).

(3) L. H. Long and M. G. H. Wallbridge, *J. Chem. Soc.*, 2181 (1963).

(4) H. G. Weiss, W. J. Lehmann, and I. Shapiro, *J. Am. Chem. Soc.*, **84**, 3840 (1962).

(5) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

(6) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

(7) J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

(8) This spectrum is assigned to poly (μ-trimethylene)diborane $(B_2C_3H_{10})_n$ (*vide infra*).

(9) In the case of IX, decoupling experiments indicate that approximately 20% smaller H_a resonance line widths are obtained if the B^{11} nuclei are irradiated with 19.2 Mc; however, fine structure is still not revealed.

(10) Long-range proton–boron coupling has been observed in dimeric dimethylaminoboron dihalides: A. J. Bannister and N. N. Greenwood, *J. Chem. Soc.*, 1534 (1965).

Table I. Chemical Shifts and Coupling Constants of Alkyldiboranes and Diborane[a]

	H^1 resonances[b]					B^{11} resonances[c]				
	Shift, τ			Coupling const		Shift	Coupling const		Assignments and comments	Ref
Compound[d]	H_a	H_t[e]	H_b[e]	J_t[f]	J_b[f]	δ[g]	J_t[f]	J_b[f]		
B_2H_6	...	6.05	10.53	135 ± 2	46.1	−17.5	135 ± 2	46 ± 2		2
$CH_3B_2H_5$	Not reported					−26.7	127 ± 5	41 ± 6	BHR	1
						−8.8	127 ± 5	48 ± 5	BH_2	
$C_2H_5B_2H_5$ (I)	9.0	5.59	10.15	132	46	−29.5	133	44	BHR	
		6.15		134		−10.0	133	46	BH_2	
n-$C_3H_7B_2H_5$ (IV)	8.60, 8.73, 8.97, 9.07, 9.17[h]	5.76	?	132	?	−28.7	134	43	BHR	
		6.37		133		−9.4	128	46	BH_2	
n-$C_4HgB_2H_5$ (VII)	8.59, 8.70, 9.00, 9.10[h]	5.52	?	128	?				BHR	
		6.14		128					BH_2	
1,1-$(CH_3)_2B_2H_4$	Not reported	...		...		−36.4	...	36	BR_2	1
						−3.6	125.5	50	BH_2	
1,1-$(C_2H_5)_2B_2H_4$ (II)	8.97	...	10.1	...	?	−40.8	...	37	BR_2	
		6.54		133		−3.9	123	48	BH_2	
1,1-$(n$-$C_3H_7)_2B_2H_4$ (VI)	8.57, 8.68, 8.97, 9.07[h]	...	?	...	?	−38.8	...	?	BR_2	
		6.52		127		−4.5	125	46	BH_2	
1,2-$(CH_3)_2B_2H_4$	Not reported					−20.5	131.2	47.5	*cis* and/ or *trans*	1
1,2-$(C_2H_5)_2B_2H_4$ (III)	9.0	5.98	9.7	129	41	−22.7	125.5	42	*cis* and/ or *trans*	
1,2-Tetramethylenediborane (IX)	8.40, 9.02	...	...	...	...	−18.6	119 ± 4	39 ± 4		4
		5.55	9.5	133	42	−22.1	129	40	This work	
1,2-Trimethylenediborane (VIII)	8.50, 8.97	5.77	9.7	130	?	−21.8	131	41	In C_6H_6	
		5.97	9.60	135 ± 12[i]	...		...	...	Polymer	
1,2-(1′-Methyltrimethylene)-diborane (X)	8.15, 8.68, 8.99	5.67	?	133	?	−22.4	132	45	In C_6H_6	
		6.0	9.62	...	...		...	...	Polymer[j]	

[a] H_a, protons of alkyl groups; H_t, terminal protons attached to boron; H_b, bridge protons attached to both borons; J_t, coupling constant H_t–B^{11}; J_b, coupling constant H_b–B^{11}. [b] 60 Mc; chemical shifts are given in τ, ppm, related to TMS as internal standard; coupling constants are given in cps. [c] 12.83 Mc; chemical shifts are given in δ, ppm, related to $BF_3 \cdot O(C_2H_5)_2$ as external standard [T. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959)]; negative values are downfield; coupling constants are given in cps. [d] Roman numerals assigned in the prior report (ref 5) are used. [e] ±0.05 ppm. [f] ±3 cps, if no other limits are given. [g] ±0.5 ppm. [h] Listed are peak positions (no first-order analysis). [i] At 80°. [j] To some extent.

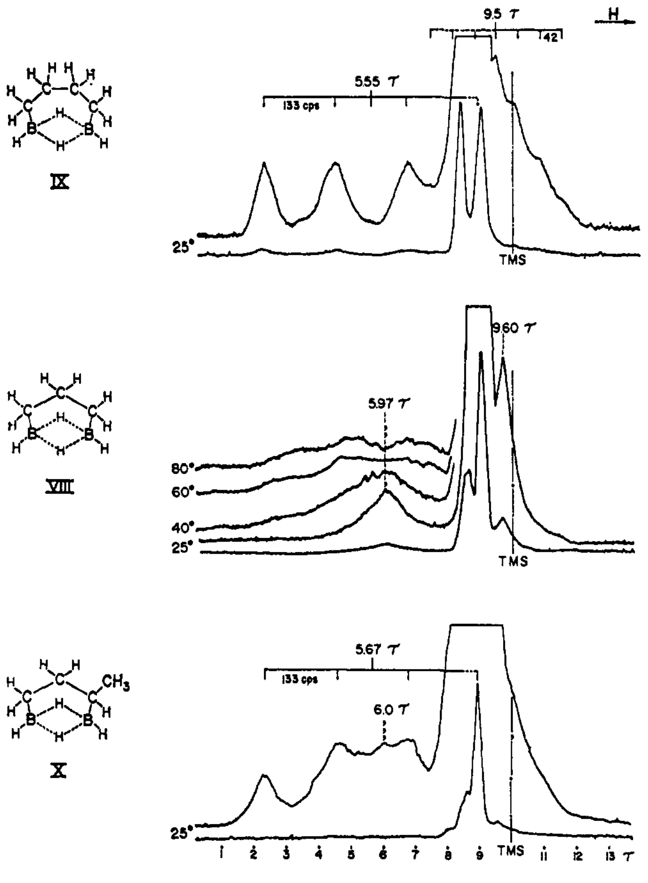

Figure 1. H^1 nmr spectra of cyclic organodiboranes (60 Mc; neat liquids; TMS (τ = 10.00) internal standard).

propene and 1-butene[5]) to carbon-attached (β-, γ-) methylene groups. From area considerations (Figure 2c,d) it is subsequently apparent that the primary mode of B–H addition to olefins is consistent with related work.[11,12]

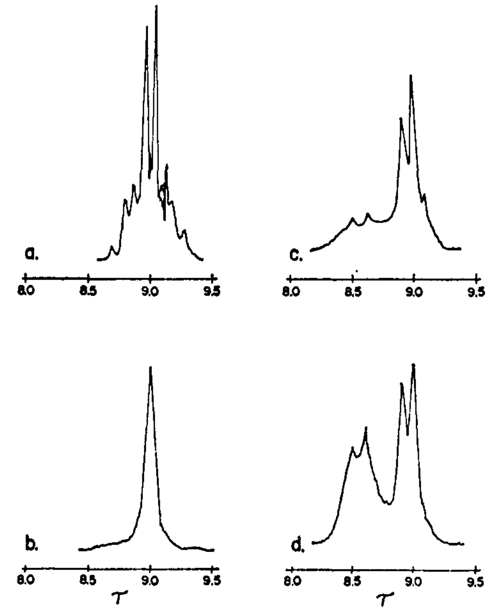

Figure 2. Alkyl proton resonances of triethylboron and alkyldiboranes (60 Mc; neat liquids; ambient temperature; TMS internal standard): (a) $B(C_2H_5)_3$; (b) $C_2H_5B_2H_5$; (c) n-$C_3H_7B_2H_5$; (d) n-$C_4H_9B_2H_5$.

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(11) R. Koester and G. Bruno, *Ann. Chem.*, **629**, 89 (1960).

(12) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

Table II. Chemical Shifts of Alkyl Protons of Alkyldiboranes and Related Systems

Compound	Chemical shift, τ^a				Internal shifts		
	α-CH_2	β-CH_2	γ-CH_2	CH_3	ΔA^b	ΔB^c	ΔC^d
1,2-Trimethylenediborane (VIII)	8.97	8.50	...	...	0.47	...	...
1,2-Tetramethylenediborane (IX)	9.02	8.40	...	...	0.62	...	...
1,2-(1′-Methyltrimethylene)diborane (X)	8.99^e	8.68^e	...	8.99^e	~0.31	~0	~0.31
Ethyldiborane (I)	9.00	...	...	9.00	...	0.00	...
1,1-Diethyldiborane (II)	8.97	...	...	8.97	...	0.00	...
1,2-Diethyldiborane (III)	9.00	...	...	9.00	...	0.00	...
n-Propyldiborane (IV)	9.07^e	8.67^e	...	9.07^e	~0.4	~0	~0.4
n-Butyldiborane (VII)	9.05^e	8.65^e	8.65^e	9.05^e	~0.4	~0	~0.4
n-Octane[f]	8.73	8.73	8.73	9.12	0.00	0.39	0.39
Tetraethylmethane[g]	8.60	...	...	9.15	...	0.55	...

[a] 60 Mc; τ values are related to TMS as internal standard. [b] $\Delta A = \Delta[\tau(\alpha\text{-}CH_2) - \tau(\beta\text{-}CH_2)]$, ppm. [c] $\Delta B = \Delta[\tau(CH_3) - \tau(\alpha\text{-}CH_2)]$ ppm. [d] $\Delta C = \Delta[\tau(CH_3) - \tau(\beta\text{-}CH_2)]$ ppm. [e] Derived from rough first-order analysis by inspection; standard deviation ±0.05 ppm. [f] Varian Associates, Spectra Catalog, Vol. 1, 1962, No. 216. [g] H. Spiescke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

The difference in ΔB between the ethyl proton resonances of $B(C_2H_5)_3$ and ethyldiboranes is readily apparent in Figure 2a,b.[13] The observed decrease in internal shift for alkyldiboranes is to be compared to a similar shift when triethylborane is converted to the trimethylamine adduct.[13] Although it is then tempting to attribute changes in ΔB to changes in boron hybridization only, the inductive effects of boron attached substituents cannot be entirely ignored. The importance of the latter effect is demonstrated in studies on the $C_2H_5BCl_2$–$C_2H_5BF_2$ pair[14] and on substituted silanes.[15]

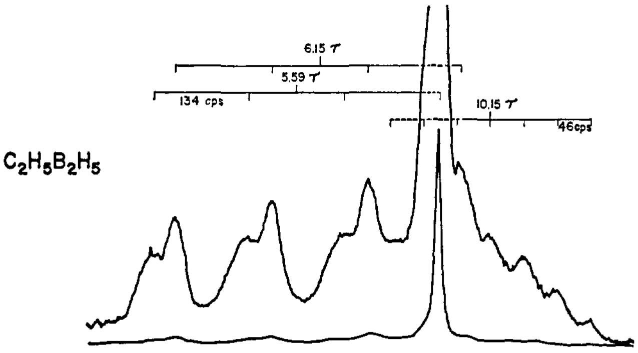

Figure 3. H^1 nmr spectrum of ethyldiborane (60 Mc; neat liquid; ambient temperature; TMS internal standard).

Resonances of Terminal and Bridge Protons Attached to Boron H_t, H_b. In proton resonance spectra, coupling of B^{11} nuclei (natural abundance 80%, $I = {}^3/_2$, magnetogyric ratio 1.366 Mc/kgauss sec)[16] to terminal and bridge protons of alkyldiboranes is normally observed as either a quartet (H_t–B^{11}, intensities 1:1:1:1) or a septet (B^{11}–H_b–B^{11}, intensities 1:2:3:4:3:2:1) which stretch out over a range of approximately 480 (at 60 Mc, τ 1.7–9.7) and 300 cps (τ 7.5–12.5), respectively (*cf.* Figures 1 and 4). As a consequence of the B^{11} quadrupole and high-field gradient in neighboring environment, the contributing peaks are in most cases very broad (half-width 45 cps) and of low intensities when recorded under conditions optimal for H_a resonances. Only by increasing the spectrum amplitude 10 to 20 times does it become possible to obtain well-defined H_t and H_b resonances.

As both experimentally observed[2] and calculated from theoretical considerations,[17] H_b nuclei of diborane resonate at considerably higher field than H_t; however, a portion of both multiplets in diborane and in substituted diboranes at 60 Mc overlap in the range of τ 7.5–9.7. In addition, the downfield half of the poorly resolved H_b septet of alkyldiboranes is normally superimposed by H_a resonances.

(a) Chemical Shifts of H_t and H_b. Relative to B_2H_6, the values of H_t and H_b (Table I) of alkyldiboranes show characteristic dependencies on the specific type of H_t–alkyl substitution. The following trends are observed.

1. Both mono- and 1,2-disubstitution of H_t by R lead to downfield shifts of the resonances of the respective remaining geminal H_t; however, the τ values for the monomer and polymer species of VIII and X differ somewhat (*vide infra*).

2. The prior effect is transmitted to the bridge protons, the resonance of which is also shifted downfield. The structural correlations are somewhat less specific than those of the H_t resonances.

3. With monosubstitution, the H_t resonance of the remaining BH_2 group is shifted to higher field. The resulting separation of the two types of terminal protons of monoalkyldiboranes is clearly demonstrated with ethyldiborane in Figure 3.[18]

4. With 1,1-disubstitution, an appropriately greater upfield shift of the remaining H_t resonance occurs.

Similar trends have been observed in the B^{11} nmr spectra of methyldiboranes.[1] The diagrams in Figure 4 correlate all data now available (Table I).

(b) H^1–B^{11} Coupling Constants (J_t, J_b). The JH_t–B^{11} ($= J_t$) and JH_b–B^{11} ($= J_b$) values of alkyldiborane show trends which reflect the degree of substitution. However, the values obtained from B^{11} nmr spectra

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[13] An internal shift, ΔB, of 0.18 ppm has been previously reported for $B(C_2H_5)_3$: R. H. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963).

[14] T. C. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

[15] H. Schmidtbauer and F. Schindler, *J. Organometal. Chem.*, **2**, 466 (1964).

[16] The B^{10} isotope (natural abundance 20%, $I = 3$, magnetogyric ratio 0.4575 Mc/kgauss sec) can generally be ignored, for each contributing peak of the H_t–B^{10} septet in the H^1 nmr spectrum is only 14% of each contributing peak of the H_t–B^{11} quartet.

[17] C. W. Kern and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 275 (1962).

[18] It is safely assumed that *cis* and *trans* hydrogens on the second boron atom have nearly the same chemical shift. If this were not the case, one-half the area of the high-field quartet at τ 6.15 would have to be assigned to H_t–B–R. This high-field assignment appears quite unlikely in that H_t–B–R resonances for other compounds (Table I) usually occur at values of at least 0.3 ppm to lower field.

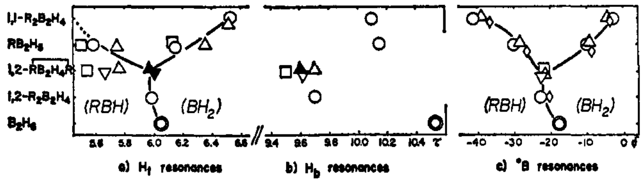
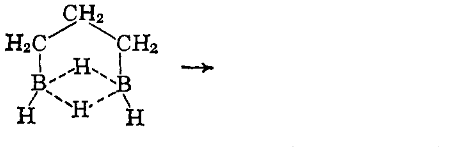


Figure 4. Chemical shifts of H_t, H_b, and ^{11}B resonances of alkyldiboranes as functions of alkyl substitution in diborane: ◇, CH_3–; ○, C_2H_5–; △, *n*-C_3H_7– or –$(CH_2)_3$–; ▽, –$CH(CH_3)$–CH_2–CH_2–; ▲, ▼, singlet resonances of the respective polymers; □, *n*-C_4H_9- or –$(CH_2)_4$–; ○, diborane.

are more precise than those derived from H^1 nmr spectra, particularly in the case of J_b. From available data (Table I), it is evident that J_t decreases slightly with increasing substitution of H_t by R, whereas J_b values demonstrate a divarication similar to the chemical shift values of H_t and B^{11} mentioned above (Figure 4a,c).

B–H Resonances of Cyclic Organodiboranes. In the spectrum of IX the observable peaks of the respective H_t quartets are well resolved, and those of the H_b septet are easily recognized. However, a comparison of the spectra for VIII, IX, and X (Figure 1) reveals a new phenomenon in that both the expected H_t and H_b multiplets of VIII and (to some extent) X have collapsed. Nevertheless, both types of hydrogens are observed as independent species, and the respective 2:2 atom ratio remains unchanged. The singlets have similar but not identical τ values with those of the expected multiplet centers. These deviations indicate that the corresponding resonances should be related to isomerizations in the underlying molecular structure. Since the τ values of the collapsed H_t quartets of both VIII and X show striking coincidences with the chemical shift of the terminal hydrogens of 1,2-diethyldiborane (Table I), the singlets are assigned to H_t resonances of a R–B_2H_4–R chain structure. Formally, such a structure is readily obtained from the somewhat strained rings of monomeric VIII (or X) by breaking and reforming bridge hydrogen bonds to yield a poly (μ-trimethylene)diborane. The relatively sharp, unsplit



$$\cdots -B_2H_4\left[(CH_2)_3-B_2H_4\right]_{n-1}(CH_2)_3- \cdots$$

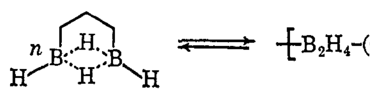
H_b singlet in the H^1 nmr spectrum of this compound supports the suggestion that diborane-like hydrogen double bridges are still present in the polymer.

The collapse of the normally observable multiplets (Figure 1, IX) appears to parallel the polymerization[5] of VIII and its C-methyl derivative, X, and should consequently be regarded as a typical indication of such a process. From comparisons of the H^1 nmr spectra of VIII and X (Figure 1) it can be concluded that the latter compound polymerizes less extensively than VIII; this is in accord with observations made during the preparation of these compounds.[5]

The assignment of H_t and H_b multiplets to monomeric cyclic organodiboranes and respective singlets to

Figure 5. B^{11} nmr spectrum of 1,2-trimethylendiborane [12.83 Mc; benzene solution; ambient temperature; δ, ppm relative to $BF_3 \cdot O(C_2H_5)_2$].

corresponding polymers is supported by four additional experimental observations. (a) Cyclic 1,2-tetramethylenediborane (IX), which has apparently much less ring strain—if any at all—than VIII and X, does not polymerize. Its H_t and H_b resonances are observed as multiplets. (b) At ambient temperature, benzene solutions of VIII show H_t and H_b multiplets. (c) The B^{11} nmr spectrum of pure VIII consists of a broad, unresolved singlet only, whereas, in accord with (b), a benzene solution of VIII reveals the tripletized doublet expected for the cyclic monomer (Figure 5; see also ref 4). (d) As shown in Figure 1, VIII, increasing temperature splits the H_t singlet into a broad quartet (as is usual, only three peaks appear uncovered by other resonances) with the expected coupling constant. The 40° spectrum was recorded immediately *after* the 80° spectrum which shows the ready reversibility of the monomer–polymer equilibrium



These observations provide sufficient evidence for the fact that coupling between H_t, H_b, and B^{11} nuclei, respectively, does not exist in polymers of the type $VIII_n$ or X_n. Furthermore, B–H multiplets are not detected in H^1 nmr spectra of polymeric organoboranes obtained by gas-phase hydroboration of 2-butyne with excess B_2H_6;[5] instead, H_t and H_b resonances are represented as singlets which are observed in the usual range of τ values, separated by 3.47 ppm (*cf.* VIII, 3.72 ppm; Table I).

Consequently, it is inferred that low viscosity and B–H coupling are associated with monomeric alkyldiboranes, whereas high viscosity and effective decoupling are found for the corresponding polymers. These viscosity dependent singlet–multiplet transitions of proton resonances appear to be the first exemplification of B–H decoupling[19] correlated to a definite change in the molecular structure.

As readily derived from the following equations, high viscosity and large molecular radii should severely affect the relaxational behavior of nuclei with electrical quadrupole moments. The spin-lattice relaxation time

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(19) Except for double resonance experiments, H^1–B^{11} decoupling was previously observed in presence of paramagnetic transition metal ions: W. N. Lipscomb and A. Kaczmarczyk, *Proc. Natl. Acad. Sci. U. S.*, 47, 1796 (1961).

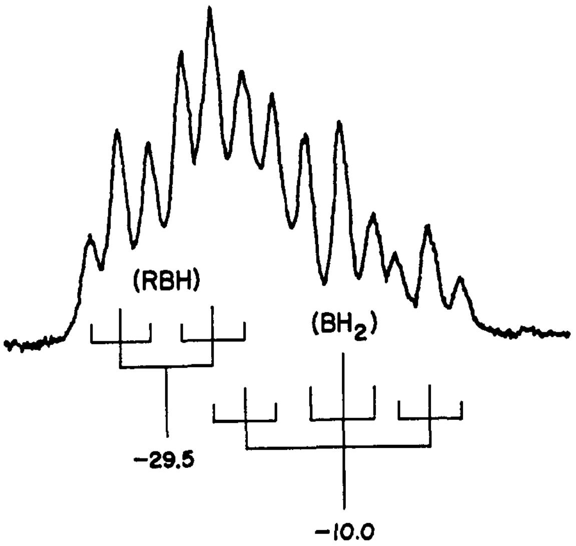

Figure 6. B^{11} nmr spectrum of ethyldiborane [12.83 Mc; neat liquid; ambient temperature; δ, ppm, relative to $BF_3 \cdot O(C_2H_5)_2$].

T_1 of such nuclei is determined[20] by

$$\frac{1}{T_1} = \frac{3}{8} e^4 h^2 q^2 Q^2 \tau_c$$

where (in the case of boron compounds) q represents the field gradient around the B^{11} nuclei, Q the quadrupole moment, and τ_c the correlation time of the molecule, respectively. The latter entity is a function of viscosity η, the molecular radius a (for idealized, spherical molecules), and temperature T.[21]

$$\tau_c = \frac{4\pi\eta a^3}{3kT}$$

Consequently, high values of η and a must lead to considerably decreased relaxation times for the boron nuclei. The different B^{11} spin states, the lifetimes of which are then considerably shortened, no longer affect the transitions of proton spin states. Therefore, as in the case when "nuclear stirring" techniques are applied, no coupling is observed; instead, a broadened singlet resonance appears. This obviously occurs with the B^{11}–H resonances of all polymeric organoboranes investigated thus far. The negative temperature coefficient[22] of the multiplicity transition, *i.e.*, singlet splitting with increased temperature,[23,24] is readily explained by the temperature dependence on τ_c.

Double Resonance Experiments. The assignments and correlations reported above on the basis of H^1, B^{11} spin–spin interactions were corroborated by decoupling experiments carried out by irradiating B^{11} nuclei at 19.2 Mc. The resulting proton magnetic resonance spectra of alkyldiboranes are considerably simplified; since all B–H multiplets collapse, the disturbing mutual overlap of the H_t and H_b resonances (*vide supra*) does not occur. In the case of the diethyldiboranes, only three singlets appear which are easily assigned to H_t, H_a, and H_b (in order of increased shielding). The interpretation of the H^1 nmr spectrum of nonirradiated, polymeric VIII (*vide supra*, Figure 4) was confirmed by comparison with the spectrum of irradiated, monomeric IX; and although both spectra were found to be very similar in over-all appearance, the characteristically different H_t chemical shift values (Table I) were again observed.

B^{11} Nmr Spectrum of Ethyldiborane. Williams, *et al.*, who reported B^{11} nmr spectra of methyldiboranes, noted that no pure sample of $CH_3B_2H_5$ was available since rapid decomposition occurred.[1] Because of the slightly greater stability of the monoethyl derivative, a much improved B^{11} spectrum was obtained (Figure 6).

Acknowledgments. The authors wish to express their gratitude to the National Science Foundation for financial support of this research. They also thank Drs. R. Keys and A. Fratiello for stimulating and helpful discussions, and W. Searcy for preparation of the drawings.

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[20] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, 216.

[21] N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948).

[22] In contrast, positive temperature coefficients of multiplicity transitions are observed if exchange processes are involved.

[23] Recently, the observed temperature-dependent B^{11} nmr spectrum of $BH_2(NH_2CH_3)_2^+$ was interpreted on the basis of nuclear quadrupole spin-lattice relaxation: S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, 87, 2756 (1965).

[24] Since N^{14} nuclei have quadrupole moments of the same magnitude as B^{11}, it is not surprising that similar temperature effects are displayed by some compounds containing nitrogen. Roberts first observed and explained on this basis T-dependent singlet–multiplet transitions of N^{14} resonances in the H^1 nmr spectra of some acylamides and pyrrolidine hydrochloride [J. D. Roberts, *J. Am. Chem. Soc.*, 78, 4494 (1956); "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p 81]. Increased viscosity with attendant quadrupole relaxation is considered to be responsible for the observed H^1 nmr spectra of formamide [A. Fratiello, *Mol. Phys.*, 7, 565 (1964)] and polyacrylamide [F. A. Bovey and G. D. V. Tiers, *J. Polymer Sci.*, 1, 849 (1963)].